indicates that the new central C–C bond of the *t*-Bu-DAT ligand is thermally resistant toward homo- and heterolytic fission.

The presented concept of selective dimerization of chiral metal units and preorganization of carbon fragments followed by C–C coupling might well be extended to the directed synthesis of functionalized dienes on small transition-metal clusters.

Acknowledgment. This research was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Scientific Research (NWO).

Registry No. 1, 123083-55-6; 2, 131704-20-6.

Supplementary Material Available: Tables of fractional coordinates of all atoms, bond distances and angles, and anisotropic thermal motion parameters for 2 and an ORTEP diagram of 2 showing 30% probability ellipsoids (7 pages); a listing of observed and calculated structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

Cycloalkyne Ligands Formed by the Coupling of Polymethylene-Bridged Alkylidynes: $L_nM{\equiv}C(CH_2)_nC{\equiv}ML_n \rightarrow L_{2n}M_2(\mu\text{-}C_2(CH_2)_n)$

Malcolm H. Chisholm,* Kirsten Folting, John C. Huffman, and Eric A. Lucas

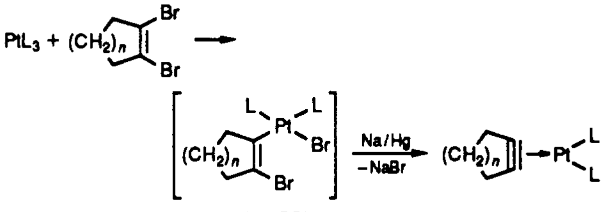
Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Received January 14, 1991

Summary: Polymethylene-bridged alkylidyne complexes $(t\text{-BuO})_3W{\equiv}C(CH_2)_nC{\equiv}W(O\text{-}t\text{-Bu})_3$ (I) have been prepared from the reactions between $W_2(O\text{-}t\text{-Bu})_6(M{\equiv}M)$ and the dinitriles $N{\equiv}C(CH_2)_nC{\equiv}N$, where $n = 3$–6, in hexane. Addition of carbon monoxide to hydrocarbon solutions of I leads to the formation of the cycloalkyne adducts $(t\text{-BuO})_6W_2(\mu\text{-}C_2(CH_2)_n)(CO)$ (II) for $n = 4$, 5 but not for $n = 3$, 6. These results are discussed in terms of the stereochemical requirements for the reversible reaction $2L_nM{\equiv}CR \rightleftarrows L_{2n}M_2(\mu\text{-}C_2R_2)$.

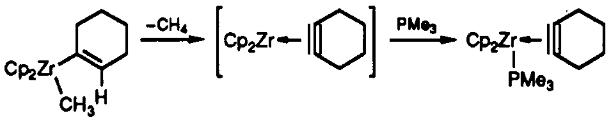
Cycloalkynes $C_2(CH_2)_n$ with small rings ($n = 3$–5) are kinetically too labile to be isolated as pure compounds.[1] They may be stabilized by coordination to metal atoms, and three routes, shown in eqs 1–3, have been developed to such complexes.[2-4] Two are similar in that they start from cycloalkenylmetal precursors, and the third involves closure of the ring in a preformed acyclic alkyne complex by carbon–carbon bond formation away from the coordinated triple bond.

We describe here a new synthetic approach for the generation of certain cycloalkyne ligands based on the coupling of two linked metal–alkylidyne moieties. This coupling reaction takes advantage of the equilibrium shown in eq 4, which is sensitive to both steric and electronic effects.[5]

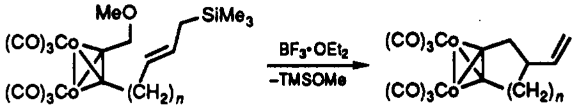


(1)

$L = PPh_3$; $n = 2, 3$

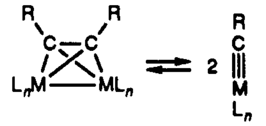


(2)



(3)

$n = 2$–4



(4)

In the present study the dialkylidyne compounds $(t\text{-BuO})_3W{\equiv}C(CH_2)_nC{\equiv}W(O\text{-}t\text{-Bu})_3$ (I), where $n = 3$–6, were prepared from the reaction shown in eq 5, a reaction based on chemistry developed by Schrock.[6] The tungsten nitride

$$2W_2(O\text{-}t\text{-Bu})_6(M{\equiv}M) + N{\equiv}C(CH_2)_nC{\equiv}N \xrightarrow[\text{hexane}]{22\ {}^\circ\text{C}} 2(t\text{-BuO})_3W{\equiv}N + \underset{\text{I}}{(t\text{-BuO})_3W{\equiv}C(CH_2)_nC{\equiv}W(O\text{-}t\text{-Bu})_3} \quad (5)$$

that forms is polymeric, is insoluble in hexane, and can be removed from the reaction mixture by filtration.[7] Re-

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[1] Greenberg, A.; Lieberman, J. F. In *Strained Organic Molecules*; Academic Press: New York, 1978.

[2] (a) Bennett, M. A.; Robertson, B. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1971**, *93*, 3797. (b) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

[3] (a) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (b) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113.

[4] Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128.

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[6] (a) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291. (b) Krouse, S. A.; Schrock, R. R. *Macromolecules* **1989**, *22*, 2569.

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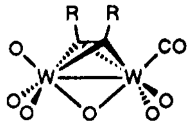
moval of solvent under vacuum then leaves the dialkylidyne as a brown material. In the case where $n = 4$, the complex is a solid and can be crystallized as tan needles that are analytically pure.[8] In the cases were $n = 3, 5, 6$, the complexes are gummy oils that could not be made to crystallize but were estimated by ^1H NMR spectroscopy to be 80–90% pure and were used in subsequent reactions.

The compounds I with $n = 3, 6$ do not react with 1 atm of CO at room temperature. However, when hexane solutions of the compounds I with $n = 4, 5$ are exposed to an atmosphere of CO, there is a slow color change from brown to blue. After about 2 days, the reaction is complete by ^1H NMR spectroscopy. Concentration of the solution under vacuum, followed by cooling to −20 °C, leads to the deposition of deep blue X-ray-quality needles of the cyclohexyne ($n = 4$) and cycloheptyne ($n = 5$) adducts, formed according to eq 6. The ^1H and ^{13}C NMR, IR, and UV–vis spectra and elemental analyses[8] of these complexes are consistent with the structure shown, which is based on that of the 2-butyne complex.

$$\underset{\text{I}}{(t\text{-BuO})_3W{\equiv}C(CH_2)_nC{\equiv}W(O\text{-}t\text{-Bu})_3} + CO\ (1\ \text{atm}) \xrightarrow[\text{hexane}]{22\ °C} \underset{\text{II}}{(t\text{-BuO})_6W_2(\mu\text{-}C_2(CH_2)_n)(CO)} \quad (6)$$



R = $(CH_3)_2$, $(CH_2)_4$, $(CH_2)_5$
O = O-*t*-Bu

The compounds II ($n = 4, 5$) both contain a crystallographically imposed mirror plane containing the W–W axis and bisecting the μ-cycloalkyne and show a disordering of the *t*-BuO ligands.[9] This disorder has been modeled with partial success ($R = 0.084$ and 0.077 and $R_w = 0.077$ and 0.072 for $n = 4, 5$, respectively), and a ball-and-stick drawing of one of the conformations of the cycloheptyne complex (II, $n = 5$) is shown in Figure 1. Because of the disorder, the structural parameters are not as precise as would be desirable. However, it is clear that each complex has a geometry very similar to that of the 2-butyne complex. The central $W_2(\mu\text{-}C_2)$ core may be considered as a dimetallatetrahedrane, with W–W = 2.637 (2) and 2.626 (2) Å, C–C = 1.42 (4) and 1.36 (4) Å, and W–C = 2.19 (2) and 2.08 (2) Å (averaged) for $n = 4, 5$, respectively. The C–C "triple" bond length is somewhat longer than that expected for a double bond,[10] and thus, the alkyne is clearly enjoying a large degree of back-bonding from the tungsten atoms. The observed back-bonding is apparently effectively more than the two-electron reduction of cyclohexyne in its zirconium complex, in which the C–C distance is 1.295 (25) Å.[3a]

The ν_{CO} value in the $\mu\text{-}C_2Me_2$ compound, 1917 cm^{-1}, is notably lower than the values for II of 1960 cm^{-1} ($n = 4$) and 1933 cm^{-1} ($n = 5$). These ν_{CO} values presumably reflect the relative π-acceptor ability of the μ-alkyne ligand, which in turn is sensitive to the C–C–CH$_2$R angle, and thus, ring size. As the ring size decreases, the C–C–CH$_2$R angle becomes smaller and the energy of the alkyne π^*-acceptor orbital is lowered, making for more favorable metal-to-alkyne back-bonding.[11]

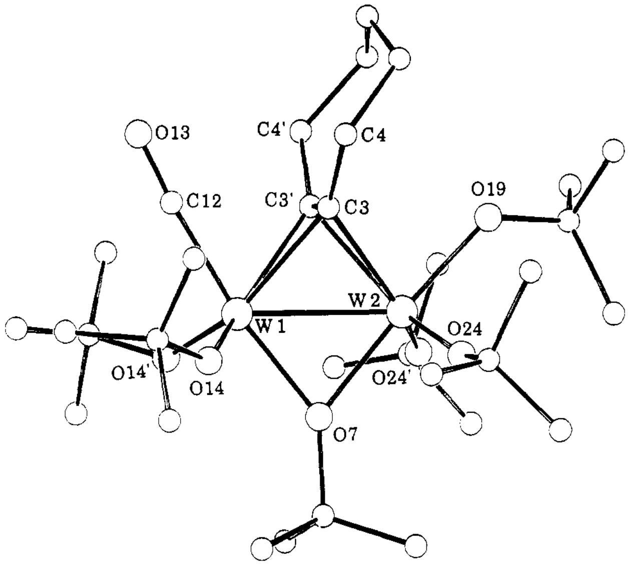
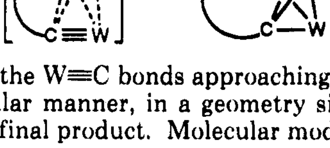


Figure 1. Ball-and-stick drawing of the μ-cyclopentyne complex $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_2(CH_2)_5)(CO)$, giving the atom-numbering scheme.

Despite the fact that the alcoholysis of the benzylidyne complex III with neopentyl alcohol in the presence of pyridine (eq 7) proceeds to give a good yield of the purple diphenylacetylene complex IV, the attempted alcoholysis of the dialkylidyne complexes with neopentyl alcohol in the presence of pyridine did not yield any tractable products. The reaction mixture turned purple after a few seconds at −78 °C but then within minutes at low temperature decomposed to give a brown solid insoluble in common solvents.

$$\underset{\text{III}}{(t\text{-BuO})_3W{\equiv}CPh} + 3Me_3CCH_2OH(NpOH) + py \xrightarrow[\text{hexane}]{22\ °C} \underset{\text{IV}}{(NpO)_6W_2(PhCCPh)(py)} \quad (7)$$

It is interesting that the CO-trapping reaction (6) only proceeds for $n = 4, 5$. Presumably this is a kinetic effect, since in the alkyne complexes the alkyne triple bonds have been effectively reduced to between a single and double bond, and such bonds in rings with $n = 3, 6$ should be relatively unstrained. It is then likely that the failure of the reaction for $n = 3, 6$ is due to the steric requirements of the ring closure reaction. For short chains, apparently the molecule is not able to attain the geometry needed for the transition state to ring closure, especially with respect to overlap between the M–C π bonds. Moreover, for large n, the linker chain begins to closely resemble a simple alkyl group as large as ethyl, for which the CO trapping (eq 6) is also known not to occur. One model for the transition state that is consistent with these facts is shown in eq 8



(8)

and involves the W≡C bonds approaching each other in a perpendicular manner, in a geometry similar to that found in the final product. Molecular models show that

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[8] Satisfactory analytical data were obtained and in all cases were low in C content by about 0.9 of a C atom per molecule, indicating partial formation of WC or W_2C in the combustion process despite the use of a combustion aid.

[9] (a) Summary of crystal data for II, $n = 4$, at −172 °C: $a = 17.331$ (4) Å, $b = 21.051$ (4) Å, $c = 10.043$ (1) Å, $Z = 4$, $d_{calcd} = 1.66$ g cm^{-3}, space group *Pmnb*. (b) Summary of crystal data for II, $n = 5$, at −154 °C: $a = 17.508$ (2) Å, $b = 21.072$ (3) Å, $c = 9.990$ (1) Å, $Z = 4$, $d_{calcd} = 1.67$ g cm^{-3}, space group *Pmnb*. Full details of the structural determination are provided in the supplementary material.

[10] *Spec. Publ.—Chem. Soc.* **1965**, *No. 18*, S14s.

[11] Hoffman, D. M.; Hoffman, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

this is likely to be unfavorable for rings with $n = 1$–3 and favorable for larger rings, whereas a parallel approach should not be prohibitive for rings as small as $n = 2$. We thus currently favor this D_{2d}-like or pseudotetrahedral transition state in the equilibria in eq 4.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Details of the experimental procedures, as well as NMR and IR spectra and elemental analysis data, for the compounds studied and listings of crystal data and refinement details, positional and thermal parameters, and bond distances and angles, as well as mono- and stereoview structural diagrams, for IIa,b (32 pages); listings of observed and calculated structure factors for IIa,b (13 pages). Ordering information is given on any current masthead page.

Cis Difunctionalization of Cyclic Olefins with Use of Organozirconium Intermediates

Gregory D. Cuny,[1a] Alberto Gutiérrez, and Stephen L. Buchwald*,[1b]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received September 19, 1990

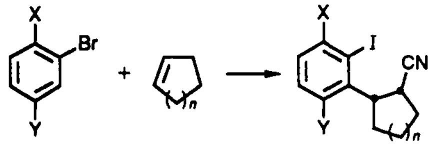
Summary: The utilization of in situ generated zirconocene–benzyne complexes as a means to effect cis carbofunctionalizations of cyclic olefins in a one-pot procedure is described. The stereospecific insertion of cyclic olefins provides the *cis*-zirconaindane metallacycles exclusively. The intermediate metallacycles were treated with a variety of electrophiles to provide diastereoselective syntheses of arylcyanoalkanes, tricyclic ketones, and 2,3-dihydrobenzo[*b*]thiophenes in moderate overall yields.

While a variety of reagents have been developed to add two heteroatoms syn to a single face of a cyclic olefin,[2] the ability to stereospecifically form two carbon–carbon bonds or a carbon–carbon bond and a carbon–heteroatom bond in a syn fashion is less common.[3] We felt that the basic approach shown in Scheme I, in which insertion of an olefin into a metal–carbon bond produces syn addition of a carbon–carbon and a carbon–metal bond, might be an attractive means to effect such cis carbofunctionalizations. We now report our initial results, in which we have used the in situ generated zirconocene–benzyne complex 1 as a means for such reactions.

Complex 1 can be generated by the addition of an aryllithium compound to zirconocene (methyl) chloride at −78 °C, followed by the thermolysis of the intermediate to effect the loss of methane (70 °C, benzene, 16 h).[4] If 1 is generated in the presence of a cyclic olefin (1.0 equiv), metallacycle 2 is the exclusive product.

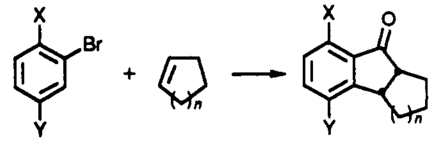
Table I

(a) Synthesis of *cis*-Cyanoarylalkanes



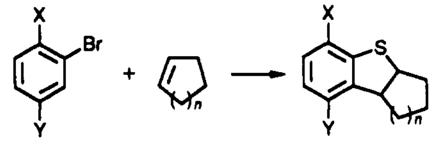
aryllithium	n	product (yield, %)
X = OMe, Y = H	1	**5** (41)
X = OMe, Y = H	3	**9** (41)
X = OMe, Y = OMe	1	**10** (41)

(b) Synthesis of Cis Tricyclic Ketones

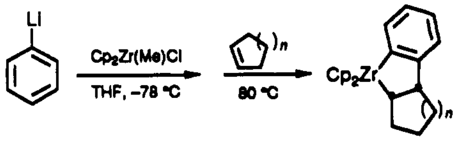


aryllithium	n	product (yield, %)
X = OMe, Y = H	1	**11** (47)
X = OMe, Y = OMe	1	**12** (40)
X = OMe, Y = H	3	**7** (56)
X = N(Me)$_2$, Y = H	1	**13** (25)

(c) Synthesis of *cis*-2,3-Dihydrobenzo[*b*]thiophenes



aryllithium	n	product (yield, %)
X = OMe, Y = H	1	**14** (52)
X = OMe, Y = OMe	1	**15** (47)
X = Me, Y = H	3	**16** (48)
X = OMe, Y = H	3	**8** (50)
X = N(Me)$_2$, Y = H	1	**17** (41)
X = Me, Y = H	1	**18** (28)



2 ($n = 1, 3$)

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[1] (a) National Science Foundation Predoctoral Fellow, 1989–1992. (b) Camille & Henry Dreyfus Teacher-Scholar Awardee, 1989–1994; American Cancer Society Junior Faculty Research Awardee, 1987–1989; Eli Lilly Grantee, 1988–1990; Alfred P. Sloan Research Fellow, 1988–1990; Union Carbide Innovation Recognition Program Awardee, 1989.

[2] Dihydroxylation: (a) Schröder, M. *Chem. Rev.* **1980**, *80*, 187. (b) Jacobsen, E. N.; Markó, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968. (c) Woodward, R. B.; Brutcher, F. V. *J. Am. Chem. Soc.* **1958**, *80*, 209. (d) Corey, E. J.; Das, J. *Tetrahedron Lett.* **1982**, *23*, 4217. Diamination: (e) Bäckvall, J. E.; Bjorkman, E. E. *J. Org. Chem.* **1980**, *45*, 2893. Hydroxyamination: (f) Sharpless, K. B.; Chong, A. O.; Shima, K. O. *J. Org. Chem.* **1976**, *41*, 177. Epoxidation: (g) Swern, D. *Org. React.* **1953**, *7*, 378. (h) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63. (i) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.

[3] Examples of cis carbofunctionalization are as follows. (a) For a review of the Diels–Alder reaction see: Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. (b) For a review of the Paterno–Büchi reaction see: Jones, G., II. *Org. Photochem.* **1981**, *5*, 1. (c) Trost, B. M.; Nanninga, T. N.; Satoh, T. *J. Am. Chem. Soc.* **1985**, *107*, 721. (d) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

[4] (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *7*, 1044. (b) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137. (c) Buchwald, S. L.; Sayers, A.; Watson, B. T.; Dewan, J. C. *Tetrahedron Lett.* **1987**, *28*, 3245. (d) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

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